PATENT SPECIFICATION

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NO DRAWINGS

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COMPLETE SPECIFICATION

Heat Treatment of Steels

We, INTERNATIONAL NICKEL LIMITED, formerly known as The International Nickel Company (Mond) Limited, a British Company, of Thames House, Millbank, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the heat-treatment of steels age-hardenable in the martensitic state. In this specificaiton the term "martensitic" is used of steels having a matrix structure composed substantially of martensite, and the term "martensite" includes low-temperature transformation products of austenite.

In many steel articles it is often necessary to harden areas or zones of the article to improve the performance under heavy stress and to give added resistance to pitting, fatigue, indentation, wear, erosion, corrosion, and other forms of damage. It is often impracticable or undesirable to give the necessary resistance to such forms of failure by making the whole article of an age-hardenable steel and then ageing it throughout to develop the necessary properties of hardness and strength. In particular, the necessary high hardness and tensile strength or compressive strength are often not obtained without sacrifice of ductility, resistance to fracture when subjected to high rates of stressing, and strength in the presence of sharp changes in section such as notches. This sacrifice throughout an article would render it more susceptible to failure under some conditions of stress. The production of an entire article in a steel of high hardness also has the disadvantage of making subsequent fabrication such as forming or machining more difficult or impossible. To overcome these disadvantages it is known to submit the zone of the article which is required to be extremely hard or strong to a process of local age-hardening.

However, difficulties may yet arise because of the need to quench the steel after a solution heat-treatment and prior to ageing. Such quenching can lead, *inter alia*, to cracking of the metal surface, particularly in articles of heavy section. Moreover when the local ageing is effected it may cause a phase change of the metal in the area treated and distortion or at least dimensional change would occur in the article. This is serious since any machining to correct this must be carried out on particularly hardened metal.

We now find that the process of local age-hardening may be applied with great advantage to steels which can be age-hardened in the martensitic state. Such steels do not require a quenching after solution-heating nor does a phase change occur during ageing in the martensitic state. Moreover the ageing can be carried out at a relatively low temperature.

According to the invention an article (or part) of a steel age-hardenable in the martensitic state is solution-heated, cooled to preserve the solution thus formed, and thereafter subjected to a localized ageing treatment to effect hardening of martensite. There are thus harder, and softer zones in the treated article, and normally it is a surface that constitutes the harder zone, but if an article requires a relatively soft surface with a relatively hard core, or one part through-hardened to a higher hardness than the remainder, appropriate differential ageing can be and is effected.

The softer zone is preferably also aged, but to a less extent. It will be understood that the localised ageing in the final state of the article may result from ageing all or most of it and then again softening a selected zone.

Differential or selective age-hardening, i.e. ageing of the selected zone without ageing of the entire component to a similar hardness, depends on setting up thermal gradients and also on the rate at which the age-hardening process proceeds at the ageing temperatures

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attained during selective hardening. It can be accomplished by locally heating the selected zone at a high rate, for example, by immersion of this zone in a hot fluidised bed or in a molten salt or molten metal bath, by flame heating, by electrical induction or by resistance heating. The necessary thermal gradients can be set up by the use of high rates of local heating, so that the remainder of the article or part remains cold, and if desired the whole article or part may be cooled to a low temperature before heating begins. Advantageously the zone that is not to be hardened may be chilled during the heating. For example, a tubular article such as a gun barrel can be cooled externally in water and heated internally, the reverse procedure being used when the external surface of a tubular article must be hard.

As is well known, ageing, the extent of which is a function of time and temperature, comprises the precipitation of a phase which had formerly been dissolved in the matrix. In general, the initial precipitates, a term which includes the so-called Guinier-Preston zones, are extremely finely dispersed, and the hardness increases with the amount of such finely dispersed precipitates that are formed. In the course of time the fine precipitates tend to agglomerate, this tendency being increasingly pronounced as the ageing temperature increases, and the agglomerates do not impart the same hardness as the finely dispersed precipitates. If the ageing is continued for too long, particularly at a fairly high temperature, the precipitates tend not only to agglomerate but also to redissolve and the steel (or other alloy) softens further. With any given reheating temperature there is thus a stage at which the hardness is at a maximum and the steel is then said to be fully aged. When this stage is passed, the steel is said to be overaged.

It may not always be possible in practice to sustain the temperature gradient or selective heating conditions for prolonged periods, and the heating conditions must be determined with proper regard to the composition of the steel. Alternatively, if the article or part in question can be made from any one of a number of steels which are age-hardenable in the martensitic state, then the steel may be so chosen that the desired change of hardness or strength is attained under specific heating conditions. It may be desirable to choose a steel which is only partly aged under these conditions, and which on being fully aged by more prolonged heating would reach a much greater hardness.

If effective use of the invention is to be made, the steel should be rich in the precipitable elements, since if it is not no great advantage i.e. difference in properties in the different zones, will be gained by means of the invention.

Broadly it may be said that any steel which is hardenable in the martensitic state should (if it is t be used in the invention) have a composition such that if it is aged at 480° C it will attain a hardness of at least 450 DPN in the course of 100 hours. It is even better if it attains a hardness of 600 DPN and better still if it attains a hardness of 700 DPN in the course of 100 hours when so aged.

The differential or selective ageing can be effected in various ways. In every case the precipitable phase must initially be in solution, so normally the first step is solution heating, but if the article has already been sufficiently heated in the course of annealing, normalising or hot-working it may not be necessary to employ a separate step of solution heating.

In the most simple treatment the whole article is first underaged to give a good combination of strength and ductility, and the zone which should be hard is further aged to a higher hardness. Normally this further ageing will involve full ageing, but if as described above the steel gives the desired hardness in a partially aged state the further ageing will not be full ageing.

Another way of effecting the differential ageing comprises overageing the zone which is required to be softer, whilst keeping cool the zone which must be harder, and then further ageing the entire article or part to bring the selected zone to high hardness and strength. This step of further ageing has little or no effect on a zone that has already overaged. In another method, which is essentially a reversal of that just described, the entire article is aged to the hardness desired for the harder zone and the zone which is required to be softer is then selectively overaged whilst the harder zone is kept cool.

It is also possible simply to heat the zone which must be harder in order to develop the desired hardness in it. The properties developed in the softer zone will then be dependent on the temperature attained as a result of the temperature gradient generated during selective heating of the harder zone. Therefore, the properties of the softer zone are subject to less control than in the previous methods.

A further method comprises overageing the whole article to give the desired lower hardness combined with reasonable ductility, and then selectively solution-heating the zone which must be hard. Thereafter the whole article is subjected to a further ageing treatment to give high hardness in the zone which was solution-heated.

In yet another way of selective age-hardening, the whole article is under-aged to give the desired low hardness and desired combination of strength and ductility, and then the zone which must be hard is selectively solution-heated and then selectively aged, whilst the softer zone is kept at a temperature

below that employed in the initial under-ageing treatment.

Any of the methods described above may be applied to steels in which precipitation does not promote a gross phase change of the matrix. However, the invention is applicable to austenitic-martensitic steels in which precipitation-hardening of the austenite can cause a microstructural phase change to martensite, which in turn can be further precipitation-hardened. These steels need special treatment.

The normal method of hardening such steels involves an initial age-hardening treatment at a comparatively high temperature, but below that of solution treatment. This treatment results in the formation of a precipitate, which in itself will harden the steel, but the formation of the precipitate denudes the matrix of alloying elements. The denuded matrix can no longer exist as austenite on cooling to low temperatures, and thus martensite is formed. This martensitic matrix is capable of further age-hardening at a lower temperature, thus supplementing the age-hardening produced in the original austenite.

Selective age-hardening of austenite-martensitic steels can be effected solely by the age-hardening of austenite; solely by the age-hardening of martensite after normal ageing and transformation of austenite throughout the entire article; or by age-hardening first the austenite and then the martensite.

To selectively age-harden only the austenite, the zone required to be softer may be kept at a lower temperature during the selective hardening, and thus will age-harden to a smaller extent, if at all, and will not necessarily transform completely or in part to martensite when cooled to room temperature or slightly below. However, merely to apply this treatment does not take full advantage of the properties of austenitic-martensitic steel, and according to the invention further ageing is effected. The way in which this is done depends on whether the desired softer zone does or does not transform substantially or completely to martensite after the selective age-hardening of the austenite. If it does, then the desired harder zone, which is essentially martensitic, should be selectively age-hardened. If however, the zone required to be softer remains substantially austenitic after selective age-hardening of the austenite, than the entire article can be subjected to the lower-temperature ageing treatment. This treatment will produce an age-hardened martensite of high hardness in the zone required to be hard, but will have little effect on the desired softer zone.

Selective age-hardening of the martensite alone in austenitic-martensitic steels can be effected by first uniformly age-hardening the austenite throughout the entire article, and then selectively age-hardening the martensite formed on subsequent cooling. The heat-treatment by which the austenite is aged can either be one that will give maximum hardness by full or substantially full ageing, or one that will produce a lower hardness, usually by overageing.

It is to be understood that, although a phase change can occur if the steel is sufficiently aged in the austenitic state and then cooled, no phase change occurs during the ageing in the martensitic state. Machining can therefore be carried out on a zone to be hardened to a high degree before the final age-hardening is effected.

The austenitic-martensitic steels include those which contain from 24 to 30% nickel, and from 1.5 to 9% in all of titanium or aluminium or both with or without other elements, as described in our Specification No. 948,355. A typical treatment of an article of such a steel to produce a hard surface with a softer core comprises solution-heating the whole article, ageing it for from 1 to 24 hours at a temperature above the martensitic transformation range and within the range of 590° C to 760° C; cooling it to below 32° C to produce a martensitic structure, and then ageing the surface for from 1/4 to 24 hours in the temperature range of 260° C to 650° C., while keeping the core cool. Preferably the temperature in the second ageing step does not exceed 540° C. These steels can be hardened to very high values, and it is advantageous therefore to use them when very high final hardness is required, even though the heat treatment is complex.

In one family of martensitic steels, the precipitatable phase is based on titanium and aluminium and the steels contain from 18 to 30% nickel together with some niobium, as described and claimed in our Specification No. 948,354. Four examples of such steels are as follows:—

Steel No.	Chemical Composition Wt. %						
	C	Ni	Co	Mo	Nb	Ti	Al
1	.039	18.29	—	—	1.06	2.0	0.45
2	.045	23.9	—	—	1.34	2.4	1.2
3	.049	20.3	—	—	1.65	1.85	0.57
4	.036	20.4	—	—	1.76	1.60	1.08

Other steels that can be aged in the martensitic state depend primarily on molybdenum and cobalt for the hardening, though additional hardening may be imparted by one or more of the elements carbon, silicon, titanium, aluminium, copper, tungsten, niobium, vanadium, beryllium, and nitrogen. These steels contain from 10 to 23% nickel, from 1 to 10% molybdenum and from 2 to 30% cobalt with or without other elements and are described in detail in our Specification No. 936,557. The hardness of these steels after ageing depends upon the content of the hardening elements, i.e. those that enter the composition of the phases precipitated on ageing, and particularly upon the contents of molybdenum and cobalt, the product of the numerical values of the percentages of which should be from 10 to 100. The steels may also contain various other elements. Such steels develop high strength when heated in the martensitic state for 3 hours at 480° C. An article of such a steel may be heated to a lower temperature, say between 300 and 400° C, for 3 hours to develop moderate hardness and then the zone to be hardened may be fully aged by rapid heating, say to 550° C for 5 minutes.

Six examples of these steels are as follows:

Steel No.	Chemical Composition, Wt. %						
	C	Ni	Co	Mo	Nb	Ti	Al
5	.023	18.9	9.90	4.9	—	0.60	0.3
6	.009	18:9	9.60	4.9	—	1.00	0.3
7	.008	18.8	9.55	4.8	—	1.71	0.3
8	.036	18.1	8.10	3.45	—	0.31	0.45
9	.004	18.1	7.90	2.9	—	0.36	1.2
10	.040	20.4	8.75	3.1	—	0.36	2.1

To exemplify the differences in hardness obtainable by differential ageing of these steels, samples of each of them were given a full age-hardening treatment comprising a solution heat treatment (1 hour at 820° C) followed by ageing for three hours at 480° C. Further samples, 0.3 inches thick, were solution-heated in the same way and aged by heating for 30 seconds at 600° C to simulate the rapid local heating of an article that occurs during a selective short-time hardening treatment by immersion in a hot fluidized bed, molten salt or metal bath, or from flame, electrical induction or resistance heating. The hardness values of the samples after each treatment are set out in the columns 1—3 of the accompanying Table and show that a substantial increase in hardness is obtained on short-time ageing at an appropriate temperature.

In certain of the methods of localised ageing described above the steel is given, after initial solution-heating and underageing, a localised solution-heating followed by ageing to harden only the solution-heated zone. To simulate this treatment a further series of samples of the steels was given a short-time solution heat treatment (30 seconds at 950° C) followed by ageing for three hours at 480° C. The hardnesses of the samples treated in this

way are set out in column 4 of the Table. Comparison of these results with those in column 2 shows that the hardness values obtained upon ageing after a short-time solution heat treatment compare very favourably with those obtained upon ageing after a full solution heat treatment (1 hour at 820° C.)

The softer portions of articles made according to the invention will generally be either in the under-aged or over-aged conditions, and for purposes of comparison the hardnesses of Steels 1—10 in these conditions are set out in the remaining columns of the Table. Column 5 gives the values obtained after solution-heating for one hour at 820° C and ageing for one hour at 350° C, which is insufficient to produce maximum hardness, and column 6, shows the values after over-ageing by heating for one hour at 650° C. Column 7 shows the hardness values obtained when this over-ageing treatment is followed by a normal ageing for three hours at 480° C. It will be seen by comparison with column 2 that these latter results are substantially lower than those that would be developed by the same ageing treatment in a zone in which the effects of over-ageing have been eliminated by a further solution-heating treatment.

The present invention is particularly applicable to the selective hardening of portions of gears, metal forming and working equipment and gun barrels as well as to the surface hardening of armour plate. A particular advantage of the invention is that the harder zone of the steels retains its hardness up to the ageing temperature, whereas the hardness of the surface layers of case-hardened steels usually falls rapidly once a temperature in the range of 150 to 200°C is exceeded.

Column No.	1	2	3	4	5	6	7
			Hardness (D.P.N.)				
Steel No.	SH 1 hr/ 820° C.	SH 1 hr/ 820° C. + 3 hr/480° C.	SH 1 hr/ 820° C. + 30 secs/ 600° C.	SH 30 secs/ 950° C. + 3 hr/480° C.	SH 1 hr/ 820° C. + 1 hr/350° C.	SH 1 hr/ 820° C. + 1 hr/ 650° C.	SH 1 hr/ 820° C. + 1 hr/650° C. +3 hr/480° C.
1	347	609	545	—	393	396	457
2	359	650	605	643	—	427	487
3	350	591	565	586	381	385	481
4	360	634	560	610	406	393	514
5	314	585	463	579	357	385	402
6	311	639	525	610	387	375	406
7	327	693	605	633	389	415	425
8	309	496	378	511	339	355	418
9	318	532	450	571	358	351	441
10	333	610	565	622	400	375	425

SH = Solution Heating.

WHAT WE CLAIM IS:—

1. A method in which an article or part of a steel age-hardenable in the martensitic state is solution-heated and cooled to preserve the solution thus formed, and thereafter subjected to a localized ageing treatment to effect hardening of martensite and render one zone harder and stronger than another.

2. A method in which an article or part of a steel age-hardenable in the martensitic state is solution-heated and cooled to retain the solution thus formed, and thereafter is subjected to differential ageing in different zones so as to harden and strengthen one zone to a greater extent than another, at least part of the differential ageing effecting hardening of martensite.

3. A method according to claim 1 or claim 2 in which the harder zone is a surface.

4. A method according to any preceding claim in which the whole article or part is first underaged to give a good combination of strength and ductility, and the zone which should be hard is further aged to a higher hardness.

5. A method according to any of claims 1 to 3 in which the zone which is required to be softer is overaged while the zone which must be harder is kept cool, and then the entire article or part is further aged.

6. A method according to any one of claims 1 to 3 in which the entire article or part is aged to the hardness desired for the harder zone and the zone which is required to be softer is then selectively overaged whilst the harder zone is kept cool.

7. A method according to any of claims 1 to 3 in which the zone which must be harder is heated in order to develop the desired hardness in it, the softer zone being heated to a lesser extent by the heat generated during selective heating of the harder zone.

8. A method according to any of claims 1 to 3 in which the whole article or part is overaged and then the zone which must be hard is selectively solution-heat treated and age-hardened.

9. A method according to any of claims 1 to 3 in which the whole article or part is under-aged and then the zone which must be hard is selectively solution-heated and then selectively aged, whilst the softer zone is kept at a temperature below that employed in the initial under-ageing treatment.

10. A method according to any preceding claim applied to an article or part of austenitic-martensitic steel in which the zone which should be harder is first selectively age-hardened in the austenitic state and then further selectively age-hardened in the martesitic state.

11. A method according to any of claims 1 to 3 applied to an article or part of an alloy according to any of the claims of United Kingdom specification No. 936,557.

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